THE ANALYST.

JUNE, 1902.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

The monthly meeting of the Society was held on Wednesday evening, May 7, in the Chemical Society's Rooms, Burlington House. Mr. W. W. Fisher, M.A., in the absence of the President, occupied the chair.

The minutes of the previous meeting were read and confirmed.

Certificates of proposal for election to membership in favour of Messrs. M. Wynter Blyth, B.A. (Cantab.), B.Sc. (London), F.I.C., and W. F. Sutherst, Ph.D. (Geneva), A.I.C., were read for the second time; and a certificate in favour of Mr. Alfred Howard, A.R.C.S., A.R.S.M., analytical chemist, 186, Stanstead Road, Forest Hill, S.E., Gas Examiner to the London County Council, and to the Lewisham Borough Council, was read for the first time.

Messrs. W. H. Jollyman, J. T. Norman, J. Golding, and W. Bowen were elected members of the Society.

The following papers were read: "The Composition of Milk," by H. Droop Richmond; "Fluorides as Butter Preservatives, with Observations on their Influence on Artificial Digestion," by Otto Hehner and C. W. Hehner; "Note on a convenient Apparatus for the Chemical and Bacteriological Examination of the Atmosphere," by Wm. Chattaway and F. M. Wharton; and a "Note on some Drug Standards," by H. Wippell Gadd.

FLUORIDES AS BUTTER PRESERVATIVES, WITH OBSERVATIONS ON THEIR INFLUENCE ON ARTIFICIAL DIGESTION.

By Otto and Charles W. Hehner.

(*Read at the Meeting, May* 7, 1902.)

The evidence taken by the Departmental Committee on the use of preservatives and colouring matters in food contains only one very brief reference to fluorides, and that of a negative character, one witness being asked whether he had met with any article of food containing fluorides, the reply being that he had not met with them, but had heard of their use.

During the last few months there appeared on the London markets a good deal of Brittany butter which either did not contain any boric preservative at all (while

the Brittany practice had hitherto been to add from 0·4 to 0·5 per cent. of boric acid), or only unusually small quantities ; yet these butters possessed the keeping qualities of butter containing preservatives. Our attention was directed to these butters by a firm of the highest standing in the butter trade. After searching for salicylic, benzoic, and sulphurous acids, with negative results, we succeeded in obtaining in a few, but by no means all such instances, distinct evidence of the presence of a soluble fluoride. Fifty grammes of the butter were melted in a platinum basin, the aqueous layer separated from the fat, rendered slightly alkaline with sodium hydroxide, evaporated, the residue ignited, transferred to a platinum crucible, strong sulphuric acid added, and the crucible covered with a waxed slip of glass upon which a distinguishing mark had been scratched with a pin. The crucible and contents were gently heated upon a sand-bath for two hours, and the glass slip examined after the removal of the wax. We found that 1 milligramme of calcium or sodium fluoride showed distinct etching of the glass.

Instead of melting the butter in a platinum basin, the melting out can be done equally well in glass, but a little alkali should be added.

It soon became apparent that in the presence of boric preservative fluoride could not thus be discovered, for in presence of both strong sulphuric acid evolves boron fluoride. By the use of dilute sulphuric acid the formation of boron fluoride is avoided, and as long as the amount of boric acid is not greater than five times that of the fluoride, a reaction (etching of the glass) can be obtained. But we found it far preferable to get rid of the boron compounds before testing for fluorides. The aqueous liquor is separated from 50 grammes of the butter, and without clarifying it calcium chloride is added, the liquid heated to boiling, and a small excess of sodium carbonate used to precipitate the calcium compounds. The precipitate consists of calcium borate, fluoride, carbonate, with some phosphate and perhaps sulphate. It is filtered off, burnt and treated with hot dilute acetic acid ; this dissolves out the carbonate, borate and phosphate. The residue is again collected on a filter, ignited, and treated with strong sulphuric acid. Distinct etching of the glass results in presence of fluoride. We have thus often been able to get fluorine reactions when, without separation of borate, the tests were quite negative. We also endeavoured to make this test a quantitative one, though with no conspicuous success. The final precipitate containing the calcium fluoride was weighed after the etching process, the sulphuric acid was driven off, the residue strongly ignited, and the weight of the resulting calcium sulphate again ascertained. Since calcium fluoride, with its molecular weight of 78 yields 136 parts of calcium sulphate, the increase of weight should furnish the measure of the amount of fluorine. But even in cases where no etching could be observed, and where we must presume fluorides to have been absent, there was a distinct residue left after the acetic acid treatment, and this, in most cases, slightly increased in weight after being converted into sulphate. It is probable that the ignited calcium phosphate was rather more insoluble in the dilute acetic acid than was expected, and tricalcium phosphate, on ignition with strong sulphuric acid, we have satisfied ourselves, gains notably in weight, the ignited residue corresponding in composition with a mixture of (calcium sulphate) and calcium pyrophosphate with a little metaphosphate. But when a fluorine reaction

was obtained, the increase in weight was nearly always materially higher than in the negative cases. The increase in weight corresponded from about 0·04 to 0·08 per cent. of sodium fluoride. This amount is probably overestimated by about 0·02 per cent., so that the actual quantity of sodium fluoride present is from 1 to 4 grains per pound. These figures make no pretence to accuracy, but cannot be far off the truth.

We obtained some of the fluoric butter preservative from Brittany. This, on analysis, was found to contain about 98 per cent. of sodium fluoride, the remainder being moisture. A strong trace of lead, doubtless due to the use of lead vessels in the preparation of the hydrofluoric acid, was also present.

With the precipitate obtained from some of the samples of butter several glass plates in succession could be strongly etched.

We have so far found fluoride in twenty samples of butter; in ten samples there was no boric preservative; while in ten others this was also present in amounts varying from 0·18 per cent. to 0·36, or from 12·6 to 25·2 grains per pound. We have also searched for fluoride in a few samples from other countries in which circumstances appeared to render the presence of some preservative other than boric likely, but with negative results. So far the use of fluoride seems to be confined to certain French butters.

As traces of fluorine must be present, and are stated to have been found, in milk, we tested the ash of 50 grammes of milk, but with quite negative results. The reactions obtained with 50 grammes of butter must therefore be due to the added material.

The Preservatives Committee of the Local Government Board recommended that borate be the only permitted preservative in butter and margarine. As, however, it might be argued that no evidence as to the use of fluorides in butter was before the Committee, the recommendation in question might not apply to that preservative, it becomes important to inquire into the physiological action of fluorides when taken in the quantities that might be consumed in butter. Taking the maximum amount we have met with—namely, about 4 grains to the pound—it would follow that in 2 ounces of butter, which a person might very easily consume, ½ grain of sodium fluoride would be contained. We take from the American Dispensatory (17th edition, p. 1634) the following statements: "Waddell states that the alkaline fluorides are not pronounced irritants, and when taken internally in doses of a grain to a grain and a half continuously they reduce the force and the frequency of the pulse, at the same time depressing the temperature and increasing somewhat the flow of urine, but not distinctly affecting either the respiratory or the cutaneous functions. This accords with the physiological studies of Tappeiner, who found in animals the soda-salt to powerfully depress blood-pressure by acting on the vaso-motor centres. Death, after profound collapse, was produced by centric failure of respiration. Dr. Waddell also affirms that there is an enormous decrease in the number of red blood corpuscles, which he believes, but does not prove, to be the result of a direct action upon the spleen."

These statements raise, to say the least, a presumption that the quantities of fluoride that are used as butter preservatives are not without injurious action upon the living body A number of experiments we have made with digestive ferments

show clearly that fluorides have, in some cases at least, a powerful inhibitory action. As regards some fermentative actions this is already well known. Thus, in Oppenheimer's book on "Ferments," translated by Mr. C. A. Mitchell, we find the statement that sodium fluoride prevents the action of rennet (p. 144), and that fluorides have a marked injurious effect upon the zymase obtained by Buchner from yeast (p. 242). In Effront's method for the suppression of bacterial organisms in the manufacture of alcohol, it has been found (Maerker, "Das Fluss-saeureverfahren in der Spiritusfabrikation," Berlin, 1891) that as little as 10 grammes of ammonium fluoride in 100 litres of water may injure the germinating power of barley, and that more than 3 grammes in 100 litres may interfere with the diastatic power of malt.

Now, since butter with about 13 per cent. of water was found to contain from 0·02 to 0·06 per cent. of fluoride, calculated as the sodium salt, the samples contained an aqueous solution of from 0·16 to 0·46 per cent. strength, which solution inhibits the growth of micro-organisms in the butter. In the experiments which we are about to give a more dilute solution was employed in every case.

Ptyalin Experiments.—Ten grammes of air-dry arrowroot were gelatinized with hot water and the bulk made up to 250 c.c.; 5 c.c. of sublingual saliva were added when the solution had a temperature of 38° C. After one hour at that temperature iodine gave only a brown coloration. The cupric reducing power corresponded to 42·63 per cent. of maltose calculated on the original starch taken.

A precisely similar experiment was made at the same time, 0·1 gramme of ammonium fluoride (containing 55·8 per cent. of fluorine) being added after the arrowroot had been gelatinized. After an hour's digestion iodine gave a strong blue colour; the solution had no cupric reducing power.

A similar experiment was made with an equivalent quantity of sodium fluoride. After one hour's digestion the solution gave a blue colour with iodine and did not reduce Fehling solution.

It follows that salivary action is prevented by a solution containing 0·04 per cent. of sodium fluoride, or its equivalent in ammonium fluoride.

Peptic Digestion.—Three lots of 50 grammes each of hard-boiled white of egg, which had been rubbed through a fine sieve, were heated to 40° C. with 250 c.c. of a 0·2 per cent. HCl solution containing enough pepsin to dissolve the whole of the white of egg. One lot did not receive any fluoride, the second 0·1 gramme, and the third 0·05 of ammonium fluoride. After five hours the whole of the white of egg in solution 1 had dissolved, the amount of egg had not visibly diminished in solution 2, while a very large proportion was left undissolved in sample 3.

It is clear that as little as 0·02 per cent. solutions of fluoride greatly interfere with peptic digestion. The difference in the appearance of the contents of the test-bottles was so striking that quantitative experiments seemed unnecessary.

Rennet Experiments.—Contrary to the statement in Oppenheimer's work, quoted above, we could not perceive any interfering action of a small amount of fluoride upon the milk-curdling action of a solution of rennet. Nor was such interfering action to be expected with quantities of fluoride smaller than amounts entirely precipitable by the calcium salts contained in the milk. As soon, however, as the calcium equivalent was overstepped, the fluoride stopped the rennet action.

Diastatic Action.—The proportions of starch (arrowroot) and water were the same as in the saliva experiments, but instead of the saliva 25 c.c. of a cold water infusion of malt were used, the temperature being maintained at 65° C. for one hour. The iodine reaction after that time was markedly different in the fluids with and without fluoride; in the former case only a darkening in the colour was the result, while in the latter a strong erythrodextrine reaction was always observed. The reducing power, calculated in percentages of maltose upon the weight of the arrowroot taken, was found to be as follows:

Without ammonium fluoride.	With ammonium fluoride.
67·4	57·4
62·1	45·0

These figures bear out Maerker's warning previously referred to. At the same time, it appears that the injurious action of fluorides upon the salivary starch-solvent action is far more pronounced than in the case of the corresponding malt-diastatic effect. From some qualitative tests made by us it also appears that the inhibitive influence of fluorides upon the ferment, which forms mustard oil from myrosin, is but slight.

Against the use of fluorides in the manufacture of alcohol, as in Effront's process, no objection can be raised from a sanitary point of view, because the chemical does not enter into the final product. The case is far otherwise when the fluoride is directly admixed with food materials and is consumed with them. At present the use of fluoride, as far as our experience goes, appears to be confined to a single country—France. We hope that our remarks may be the means to arrest the further spread of its employment.

We may further take this opportunity to express the hope that the President of the Local Government Board will no longer delay the issue of regulations concerning the use of preservatives, the Committee's report having been presented nearly six months ago.

Discussion.

Mr. Lloyd said that about fifteen years ago he had been told by the agent of one of the colonies that a means of preserving butter had been discovered which could not be detected by analysis, and, after much trouble, he had found that fluorides were being used. He had reported that fluorides were far more injurious than some other preservatives, and, as far as he knew, they were given up in favour of boracic acid. Last year, however, he had been informed that in Brittany fluorides, in the form of sodium fluoride, were again being used, and he regretted to say that, as soon as the possibility of the prohibition of the use of preservatives in England became known, the material was introduced on this side of the Channel. Moreover, he was afraid that its use might not be confined to butter. The Preservatives Committee had recommended that the use of $\frac{1}{2}$ per cent. of boracic acid should be permitted in the case of butter—a substance which had been washed free from the constituents causing decomposition—and that $\frac{1}{4}$ per cent. should be allowed in the case of cream, which was much more difficult to preserve than butter, for the

substances liable to decomposition, instead of being washed out, were all contained in it. So far as he knew, sodium fluoride was being used—or, at any rate, was ready to be used—not merely for butter, but for milk and cream. He thought that a debt of gratitude was due to the authors of this paper for having described so clearly a method by which it could be detected. It had taken him a very long time, in years gone by, to detect the preservative in the colonial butter he had referred to, and if he had not been perfectly certain that some preservative was present, he might have considered the search hopeless, and have said that no preservative was present. In regard to the statement that the action of fluorides upon rennet was only marked when sufficient was present to neutralize or combine with the lime present in the sample of milk experimented with, he would point out that the action of rennet was a time action, and the question was not whether the action might be actually stopped, but whether it might not be delayed; and he would like to hear whether the authors had made any experiments which would show whether the action of rennet was delayed to any extent by quantities of fluorides too small to stop it altogether, for he fancied that the digestion of milk in the infant must be to some extent similar to the action of rennet, and therefore that a substance added in small quantities, if it delayed the action of rennet, would probably also delay digestion in the infant, and would, on that account, be injurious, although it might not actually prohibit entirely the action of rennet.

Mr. Allen said that probably it was within the knowledge of the authors and of others present that the use of silico-fluoride of sodium as a preservative had been patented, and that the compound was manufactured to a considerable extent at Warrington. The use of sodium fluoride had probably grown out of it. It was interesting, seeing that the association of boric acid with fluorides had been mentioned, to note that boron compounds also were manufactured largely at Warrington. He would like to hear if the authors had any suspicion that the two were used in conjunction. Possibly the boron was in the form of boro-fluoride of sodium ($NaBFl_4$); or borax and hydrofluoric acid might be used, and would probably form a compound ($HBFl_4$) eminently suitable for the purpose in question.

Mr. Richmond mentioned that it had been proposed to use fluo-boracic acid as a preservative, and some years ago he had examined a sample which contained it. He did not think, however, that it had ever been extensively used.

Mr. Briant said that sodium fluoride had been patented some five or six years ago as a preservative for beer, but in that case, again, no practical application had followed.

Mr. Fisher said that he remembered that some years ago potassium boro-fluoride had been recommended as a strong and powerful antiseptic and an excellent preservative, and he had made a few experiments with it at the time, but he had never met with it professionally, and did not know that it had come into use.

Mr. O. Hehner, in reply, said that their experiments had been confined to ascertaining the presence of fluorides, and he could not say whether boro-fluoride had been also used or not. In many cases boro-fluoride was certainly absent, for they had found fluoride in the absence of boron. He doubted whether at the present

time any Australian butter contained fluorides. Their experiments in regard to the action of rennet were quite qualitative. The results obtained had been that without fluorides coagulation took place in a very short time at blood heat, while after the addition of fluorides the milk remained fluid for a long time. The inhibitive action of the fluoride was only apparent after a certain quantity had been added. The first few drops of the solution, which made no difference, were, he surmised—though he had not actually determined whether such was the case—necessary for the precipitation of the calcium. Their remarks had been intended mainly for the nformation of analysts, but partly also for the information of the Board of Agriculture. He presumed that the limitations recommended by the Departmental Committee on Food Preservatives could only be regarded as extending to those preservatives which had been referred to in the course of the Committee's inquiry. Only such substances could be prohibited or permitted as were known to be used at the time of the inquiry. As, however, formal regulations had not yet been issued, there might be still time to extend the prohibition to fluorides, which, in his opinion, were njurious.

THE RAPID ESTIMATION OF BORIC ACID IN BUTTER.

By H. Droop Richmond, F.I.C., and J. B. P. Harrison, F.I.C.

(*Read at the Meeting, April* 9, 1902.)

The report of the Preservatives Committee recommending a limit of 0·5 per cent. of boric acid in butter has rendered it desirable to make the estimation of this substance as simple and rapid as possible. We have been in the habit of using a slight modification of Thomson's method: About 25 grammes of butter is weighed into a stoppered cylinder, enough water to make with the water already present a number of c.c. equal to the weight of butter in grammes, and 10 to 15 c.c. of chloroform are added; the contents of the cylinder are warmed, mixed, and allowed to separate; an aliquot portion of the aqueous solution is drawn off (each c.c. containing the boric acid of 1 gramme of butter), made alkaline, evaporated, ignited, and the soluble ash dissolved in hot water. This solution is made neutral to methyl orange, boiled to expel CO_2, and, after the addition of glycerol, titrated with standard alkali. We have proved the accuracy of this method, have found that the insoluble ash is free from boric acid, and have also ascertained that the ignition cannot be dispensed with, the results without it being from 0·05 to 0·10 per cent. too high.

The evaporation, ignition, and extraction of the ash with hot water take up some little time, and we experimented to find a method which would avoid this. Our first experiments were with a slight modification of Deniges' method for the estimation of boric acid in milk (*J. Pharm. Chim.*, vi. (2), 49), but we failed to obtain sufficiently concordant results, due, as we soon found, to the fact that the end-point, when titrating boric acid with phenolphthalein in milk-sugar solution, varied greatly with the temperature. We found, however, that when the solution was boiling the end-point was constant and sufficiently sharp. The end reaction is distinctly sharper in

milk-sugar solution than in water; a 5 per cent. solution of milk-sugar was somewhat arbitrarily adopted.

Our preliminary experiments were made with a weighed quantity of boric acid dissolved in 10 c.c. of water, to which was added 15 c.c. of a 10 per cent. milk-sugar solution and 3·25 c.c. of water (the average amount contained in 25 grammes of butter). A few drops of phenolphthalein were added, and the solution raised to the boiling-point; $\frac{N}{2}$ caustic soda solution was added till a faint but distinct pink colour was observed; about 15 c.c. of glycerol was then added, and the solution titrated until a pink colour was produced.

The following results were obtained:

Boric Acid taken.	C.c. of $\frac{N}{2}$ Soda in Milk-sugar Solution.	C.c. $\frac{N}{2}$ Soda in Glycerol Solution.	Difference.	Boric Acid found.
0·100	0·53	3·23	2·70	0·099
0·070	0·33	2·24	1·91	0·070
0·050	0·26	1·62	1·36	0·050
0·020	0·10	0·65	0·55	0·020

It is seen that the difference between the two titrations indicates 84·4 per cent. of the total boric acid, and 1 c.c. of $\frac{N}{2}$ soda is equal to 0·0368 grammes of boric acid.

The influence of slight dilution was studied; a 1 per cent. boric acid solution was used.

Ten c.c. boric acid solution + 15 c.c. 10 per cent. milk-sugar solution + 0 c.c. water, indicated 0·100 gramme boric acid.

Ten c.c. boric acid solution + 15 c.c. 10 per cent. milk-sugar solution + 3·25 c.c. water indicated 0·100 gramme boric acid.

Ten c.c. boric acid solution + 15 c.c. 10 per cent. milk-sugar solution + 7·5 c.c. water indicated 0·098 gramme boric acid.

The dilution due to the extreme percentages of water likely to be met with in butter will not affect the determination.

Various substances which may occur in butter were added to the boric acid solution.

Ten c.c. boric acid solution + 15 c.c. 10 per cent. milk-sugar solution + 4 c.c. milk indicated 0·100 gramme boric acid.

Ten c.c. boric acid solution + 15 c.c. 10 per cent. milk-sugar solution + 3·25 c.c. of a solution containing butyric and caproic acids indicated 0·100 gramme boric acid.

Ten c.c. boric acid solution + 15 c.c. 10 per cent. milk-sugar solution + 3·25 c.c. of a solution containing 0·030 gramme P_2O_5 indicated 0·102 gramme boric acid.

Ten c.c. boric acid solution + 15 c.c. 10 per cent. milk-sugar solution + 3·25 c.c. of a solution containing 0·059 gramme P_2O_5 indicated 0·102 gramme boric acid.

It is thus seen that none of the substances likely to be present in butter will affect the determination. Considerable quantities of phosphoric acid have, however, a prejudicial effect; a solution free from boric acid, and containing 0·297 gramme P_2O_5, indicated 0·019 gramme of boric acid.

Mixtures of boric acid and borax may be titrated by adding a little mineral acid to liberate boric acid from the borax.

An amount of commercial preservative equal to 0·100 gramme of boric acid indicated 0·103 gramme boric acid.

As the result of our experiments, we have adopted the following method: Weigh out 25 grammes of butter in a beaker, add 25 c.c. of a solution containing 6 grammes of milk-sugar and 4 c.c. N sulphuric acid to 100 c.c. Place in the water-oven till the fat is just melted and stir well; allow the aqueous portion to settle for a few minutes and draw off 20 c.c.; add a few drops of phenolphthalein, bring to the boil, and titrate with $\frac{N}{2}$ soda till a faint pink colour just appears; add 12 c.c. glycerol, and titrate till a pink colour appears. The difference between the two titrations, less the amount of alkali required by 12 c.c. of glycerol, multiplied by 0·0368, will give the amount of boric acid in 20 c.c., and this, multiplied by

$$\frac{100 + \text{percentage of water}}{20},$$

will give the percentage. If the percentage of water is about the average, it may be taken as 13 without appreciable error.

Generally, the number of c.c. of $\frac{N}{2}$ soda used, multiplied by 0·2, will very closely approximate to the percentage of boric acid.

The following test experiments will show that the method is accurate enough for all purposes. They were made by weighing out 25 grammes of butter free from boric acid, adding a known weight of boric acid or a commercial preservative of known boric acid value, and estimating as already described:

Boric Acid added. Per Cent.	Boric Acid found. Per Cent.	C.c. $\frac{N}{2}$ Soda $\div 0{\cdot}2$
0·10	0·11	0·11
0·25	0·26	0·25
0·35	0·36	0·35
0·45	0·46	0·44
0·56	0·55	0·52
0·62	0 60	0·58
0·88	0·86	0·84

Butters free from boric acid have shown a difference between the two titrations equal to the amount of alkali required by the glycerol. We communicated the method to Mr. Hehner, and at his request Mr. B. W. J. Warren has sent the following results to us:

Boric Acid added. Per Cent.	Boric Acid found. Per Cent.
0·48	0·50
0·60	0·59
0·67	0·70
0·47	0·46
0·11	0·13

Mr. Warren also found in another butter 0·45 per cent. in daylight, and 0·44 and 0·42 per cent. by gaslight.

Discussion.

Mr. B. W. J. Warren said that one difficulty he had met with in his experiments referred to in the paper was the production of a pink colour, which rendered one very liable to overshoot the mark in titrating. He had found, however, from some investigations of Mr. R. T. Thomson, that lacmoid would answer a similar purpose to methyl orange, and he had accordingly experimented with lacmoid, and had obtained very good results. The lacmoid could be easily seen in the turbid solution obtained from the butter.

Mr. F. J. Lloyd inquired why a solution of milk-sugar was used. He had made estimations simply by extracting with boiling water and filtering, and had found no difficulty in obtaining accurate results without using a solution of milk-sugar—simply adding the sulphuric acid and boiling.

Mr. Richmond hoped that the very interesting information which Mr. Warren had given with regard to the use of lacmoid, which was certainly more convenient to use than phenolphthalein, would be embodied not merely in a short note in this discussion, but in a paper before the Society, going more fully into the details of the method, and giving the results obtained. Mr. Warren's method appeared, as far as he could see, to be better than their own, and he should try it at once. Before answering Mr. Lloyd's question, he would like to hear exactly how Mr. Lloyd obtained the result he mentioned with water—whether he titrated, first of all, with methyl orange and then with phenolphthalein and glycerol, or simply, as they had, first titrating, till the pink colour appeared, with water, then adding glycerol, and going on with the titration and taking the difference.

Mr. Lloyd said that the titration was made first with methyl orange, and then with phenolphthalein and glycerol, methyl orange being used before the addition of the glycerol.

Mr. Richmond said that in that case he could hardly understand Mr. Lloyd getting accurate results, because there must be a certain amount of casein and other proteids in the aqueous portion, as well as a certain amount of phosphoric acid in the form of phosphates. These two both interfered when methyl orange and phenolphthalein were both used, because the end-points for methyl orange and for phenolphthalein were very different. That was the reason for stating in the paper that evaporation and ignition could not be dispensed with, the results otherwise being from 0·05 to 0·1 per cent. too high. The reason for using milk-sugar was that they had found that with milk-sugar, in boiling solution, the end-point was sharper than was the case in an aqueous solution simply. The true reason was that the amount of dissociation was more sharply determined in the milk-sugar solution than in the aqueous solution, the practical result being that the end-point was easier to see.

A CONTRIBUTION TO A KNOWLEDGE OF THE CHEMISTRY OF CIDER.

By Alfred H. Allen.

(*Read at the Meeting, December* 11, 1901.)

Cider is well known to be prepared by the alcoholic fermentation of apple-juice. Skilful manufacturers maintain that the juice itself is all that is needed for the production of a perfect article, the processes being of the simplest kind:—namely, the preparation of the juice by pressing the sliced or grated apples; exposure of the juice at a temperature of or near 60° F., when it undergoes spontaneous alcoholic fermentation; and the removal of the dregs and scum, which form in considerable quantity, by racking as often as may be necessary, supplemented in some cases by filtration of the liquid. Sometimes catechu or other tannin matter is employed to precipitate albuminous matters, occasionally anti-acids are used to correct undue acidity, and preservatives, especially salicylic and boric acids, are stated to be frequently employed. An extensively-advertised preservative of cider, which I purchased in Bristol, was found on analysis to consist of calcium sulphite. According to Mr. G. Embrey, in Gloucestershire, an addition of 1 quart of milk to 18 gallons of cider is often made for fining the liquid, and as a preservative salicylic acid is frequently used in a proportion of 1 ounce to 96 gallons.

The apples suitable for the manufacture of cider are in many cases grown especially for the purpose, and are somewhat unpalatable, as they contain considerably more tannin than ordinary table apples. Ordinary table apples are unsuited for the production of cider, and, in fact, but few varieties of apple can be advantageously used alone, the practice of skilled cider-makers being to employ a mixture of different kinds of apple, so that the excess of certain constituents in some kinds may compensate for the deficiency in others.

Among the most esteemed cider-apples of the South-west and West of England are the Fox Whelp, Royal Wilding, Sweet Alfred, White Normandy Beech, Tom Put, White and Yellow Styres, Handsome Mandy, Kingstone Black, and Skyrme's Kernel.

In America, cider is made from the Baldwin, Newtown Pippin, Sweet Vandever, Rosebery Russet, Rambo, and many other varieties of apple, some of which are ill-suited for the purpose.

There is no doubt that in some parts of England the apple-trees have been so neglected that their fruit has degenerated, and contains an abnormal proportion of acid. The trees in some districts are rarely, if ever, pruned or manured, and the apples—windfalls, ripe and rotten fruit together—are allowed to remain in the orchard for many weeks, in some cases not even being stacked or protected from pollution by animal excreta. Starting with a mixture of unripe and more or less damaged fruit, with possible admixture of foreign matters, it is not surprising that the cider made and consumed by the rural population of the cider districts is apt to be of very inferior quality. The manufacturers of cider for public sale, of course,

proceed in a more systematic manner, but they are largely dependent on the defective fruit described above. Cider is, however, now manufactured in England in increasing quantities under conditions in which the above defects are carefully guarded against, and a product of unexceptionable quality results.

Opinions as to the effect of apple-pips on the quality of cider vary greatly. Some cider manufacturers aim at crushing them, while others as carefully avoid doing so.

It is not generally recognised that under the generic term "cider" are grouped a number of products of the fermentation of apple-juice, which products vary among themselves almost as greatly as the numerous products from the fermentation of grape-juice grouped together under the generic name of "wine." Yet no distinctive names are given to the different classes of cider, except such as "sweet," "dry," "sparkling," etc. The geographical origin allows of some differentiation in the character of cider, but the terms "Devonshire," "Herefordshire," "American," etc., have not the same definite meaning that attach to the names Burgundy, Bordeaux, Champagne, Port, etc., in the case of wine. The proportion of sugar varies in cider from 10 to less than 1 per cent., diminishing with the age, while the proportion of alcohol increases. A serious practical difficulty in the classification of cider is its tendency to undergo both alcoholic and acetic fermentation in addition to more obscure changes, so that it is very difficult to insure that any particular brand shall be of approximately constant character.

In the case of sweet cider, which is necessarily only partly fermented, the proportion of alcohol is generally too low to preserve the liquid from further change, and hence a foreign antiseptic agent, such as salicylic or boric acid, is sometimes added. A "dry" cider, in which more perfect fermentation has occurred, is to be preferred on several grounds, but the manufacture of a natural product of this kind presents considerable difficulties, and the demand for it is limited. As long as the cider contains a fair proportion of sugar the sweet taste masks the presence of any excess of acid, but in dry cider this becomes unpleasantly apparent, unless some supplementary treatment be adopted.

The following table shows the chief constituents of *apples* analysed in my laboratory:

TABLE I.

	TABLE APPLE.	COOKING APPLE.	CIDER APPLES.	
	Blenheim Orange.	Derby.	Sweet Alfred.	Tom Put.
Water	81·62	84·74	80·29	84·14
Free acid (as malic) ...	0·88	0·56	0·097	0·36
Glucose	9·28	8·75	9·43	7·21
Sucrose	6·28	2·29	2·95	2·84
Ash	0·44	0·33	0·54	0·44

Many published analyses of apples and apple-juice are misleading, owing to the observers having ignored the presence of non-reducing sugars. Such sugar (presumably sucrose) is always present, and sometimes in considerable proportion. When the fruit is over-ripe the proportion of sucrose diminishes, a portion of it undergoing inversion, though part apparently undergoes a less simple change. The following figures, obtained in my laboratory, show the change resulting from decay in the case of two typical Devonshire cider-apples. The decayed portions were carefully separated from the still sound parts of the fruits, and each fraction analysed separately.

	No. 1 Apple.		No. 2 Apple.	
	Sound Part.	Decayed Part.	Sound Part.	Decayed Part.
Moisture	80·50	81·68	—	—
Volatile acid	0·016	0·057	—	—
Fixed acid	0·109	0·436	—	—
Glucose (reducing sugar) ...	9·30	11·86	9·49	11·61
Sucrose (non-reducing sugar) ...	6·67	1·49	4·74	0·98

The composition of the pressed apple-pulp, or *marc*, obtained in large Devonshire cider factories is shown by the following figures. In the cases of the first three samples the apples had been pressed once only, but in the case of the fourth the pulp had been broken up and re-pressed:

	1	2	3	4
Moisture	68·14	68·14	75·62	63·36
Glucose	4·04	—	4·69	2·24
Sucrose	2·14	—	2·26	1·88
Ash	—	1·01	1·03	1·71

The large proportion of water in apple-marc renders any useful application of the product very difficult. To a limited extent, and when quite fresh, it is sometimes employed as a cattle food, in other instances it is burnt under boilers fitted with a special contrivance, and in other cases it is taken out to sea.

The following table shows the variation (grammes per 100 c.c.) in the chief constituents of *apple* and *pear juice* from various parts of France, as recorded by Truelle:

Table II.

	Apple Must.			Pear Must.		
	Minimum.	Maximum.	Average.	Minimum.	Maximum.	Average.
Specific gravity ...	1057·5	1110·0	1076·0	1067·5	1098·0	1084·5
Total solids calculated from specific gravity	14·94	28·57	19·74	17·53	25·32	21·95
Acidity (as H_2SO_4) ...	0·07	0·74	0·21	0·08	0·24	0·15
Sucrose	0·56	7·17	2·50	1·67	6·14	3·67
Glucose	10·84	18·18	13·58	10·81	20·99	14·56
Pectous and albuminous matters ...	—	2·3	1·2	0·3	1·8	1·31
Tannin	0·026	0·81	0·29	0·10	0·32	0·18

The following results show the composition of fresh *apple-juice* as used for the manufacture of cider in the South-west of England. The formation of alcohol occurs very rapidly, and hence a notable proportion was found in several cases, though the analysis was commenced within thirty-six hours of the apples being pressed.

TABLE III.

	A.	B.	C.	D.	E.
Specific gravity	1·0550	1·0530	—	1·0470	1·0470
Alcohol, present by weight ...	0·10	—	—	1·04	1·13
Total extractive matters ...	14·63	12·74	16·11	11·91	11·95
Glucose	(13·51)	10·48	12·50	9·13	8·82
Sucrose	1·34	0·69	—	0·66	0·38
Fixed acid (as malic)	0·28	0·42	0·12	0·45	0·50
Ash	0·35	0·30	—	0·22	0·26
Tannin	—	0·22	0·11	—	—
Original solids	14·84	12·74	16·11	14·05	14·28

The next three tables show the results yielded by the analysis in my laboratory of typical English ciders.

TABLE IV.

Analysis of Six Varieties of Norfolk Bottled Cider.

	A.	B.	C.	D.	E.	F.
Specific gravity ...	1·005	1·002	1·012	1·012	1·012	1·002
Alcohol, by weight ...	5·30	7·21	6·56	7·29	7·14	7·69
= Proof spirit ...	11·60	15·72	14·34	15·88	15·57	16·73
Grammes per 100 c.c. Total extractive matters ...	2·07	2·54	4·71	5·47	4·55	2·33
Glucose ...	0·77	1·16	4·16	4·55	3·12	0·88
Fixed acid (as malic) ...	0·35	0·42	0·39	0·42	0·41	0·31
Volatile acid (as acetic) ...	0·07	0·21	0·15	0·11	0·10	0·10
Ash	0·30	0·26	0·31	0·33	0·27	0·26
Original solids ...	13·09	17·71	18·45	20·65	19·41	18·32

TABLE V.

Analysis of Typical Samples of Devonshire Bottled Cider.

	G.	H.	I.	J.	K.	L.	M.*	N.*	O.	P.	Q.
Specific gravity	1·012	1·003	1·013	1·006	1·032	1·011	1·029	1·0275	1·0230	1·0260	1·0190
Alcohol, per cent. by weight ...	4·77	5·39	5·09	4·95	2·57	4·09	4·01	3·77	4·18	3·43	4·62
= Proof spirit	10·44	11·79	11·14	10·82	5·63	8·96	8·79	8·28	9·16	7·53	10·13
Total extractive matters	4·09	2·80	4·27	2·12	8·23	3·88	7·77	7·93	7·13	7·73	6·25
Glucose ...	2·94	1·43	2·27	0·94	7·24	2·17	6·76	6·85	5·62	5·68	4·90
Fixed acid (as malic) ...	0·15	0·19	0·33	0·12	0·31	0·21	0·30	0·33	0·35	0·34	0·22
Volatile acid (as acetic) ...	0·19	0·32	0·24	0·20	0·37	0·31	0·30	0·23	0·24	0·20	0·28
Ash	0·23	0·29	0·34	0·25	0·34	0·30	0·27	0·25	0·31	0·41	0·36
Original solids	14·20	14·39	15·12	12·62	14·08	12·77	16·48	16·05	16·10	15·10	16·19
Total sugar (as glucose) ...	—	—	—	—	—	—	—	—	6·25	6·76	5·10

* A small quantity of sugar solution was added to these ciders.

TABLE VI.

Analysis of English Draught Ciders of Good Quality.

	R.	S.	T.	U.	V.	W.
Specific gravity ...	—	1·012	1·027	1·016	1·006	1·028
Alcohol, per cent. by weight	5·86	3·96	3·86	4·06	4·37	2·49
= Proof spirit ...	12·83	8·68	8·47	8·90	9·58	5·47
Grammes per 100 c.c. — Total extractive matters ...	7·63	3·04	8·14	5·18	2·59	7·52
Grammes per 100 c.c. — Glucose ...	—	—	4·17	2·94	0·93	6·17
Grammes per 100 c.c. — Sucrose ...						
Grammes per 100 c.c. — Fixed acid (as malic) ...	0·41	0·43	0·26	0·31	0·25	0·20
Grammes per 100 c.c. — Volatile acid (as acetic) ...	0·21	0·18	0·16	0·18	0·20	0·23
Grammes per 100 c.c. — Ash	0·22	0·22	0·34	0·24	0·35	0·24
Original solids ...	20·01	11·47	16·39	13·81	11·89	12·99

The following is an epitome of an elaborate research on the composition of French ciders by Eugene Grignon (*Le Cidre*, Paris, 1887). The figures for alcohol are given in c.c. per 100 c.c. of cider, but the other figures (given originally in grammes per litre) are expressed in grammes per 100 c.c. of the cider. The samples in Columns A and C were made from pure apple-juice, without any addition of water. Samples in Columns B and D were ciders to which known proportions of water had been added, and were consumed in the districts in which they were produced; but the figures in the table are corrected for the water added, and so represent undiluted ciders. Column E shows the composition of "renourris" ciders from the Department of the Eure. These are ciders five or six years old, which have received annually an addition of must sufficient to make up for the loss by evaporation. They are relatively rich in alcohol and low in extractive matters, the pectous bodies undergoing gradual precipitation.

To the actual results of analysis, Grignon appends the calculated amounts of alcohol and extractive matter which would be found in the cider if it had undergone complete fermentation. This is effected by deducting 0·1 per cent. from the sugar found by analysis (as an allowance for matters other than sugar which reduce alkaline copper solution, and are not removed by a preliminary treatment with basic lead acetate), and multiplying the difference by 0·6117, on the ground that 100 grammes of invert sugar yield on fermentation 61·17 c.c. (= 48·55 grammes) of alcohol. Thus, if a sweet cider contain 4·0 per cent. of alcohol (by volume) with 6·64 grammes per 100 c.c. of total extract, including 3·57 of sugar, then the completely fermented liquid will contain 6·12 c.c. of alcohol and 3·17 grammes of extract per 100 c.c.*

An additional allowance might advantageously be made for the acetic acid present in sour cider. Each gramme of this corresponds very nearly to 1 c.c. of alcohol.

The free acid of the cider is stated by Grignon in terms of sulphuric acid, instead of the fixed acid being calculated as malic and the volatile acid as acetic acid. One c.c. of normal alkali will neutralize 49 milligrammes of H_2SO_4, 60 of $HC_2H_3O_2$, or 67 of $H_2C_4H_4O_6$, so that no large error results from the fact that the fixed and volatile acids are not differentiated. In the following tables I have added to Grignon's figures a statement of the original solids of the juice, but in calculating them I have made a constant allowance of 0·2 per cent. for sugar lost from the extract through acetic fermentation.

* 3·57 of sugar found, minus 0·10, leaves 3·47 of corrected sugar in sample. 6·64 of extract, minus 3·47, leaves 3·17 extract in the completely-fermented cider. 3·47 of corrected sugar, multiplied by 0·6117, gives 2·12 increase in alcohol, which, added to 4·00 in original sample, gives 6·12 c.c. of alcohol per 100 c.c. of completely-fermented cider.

TABLE VII.

Analyses of French Ciders (E. Grignon).

	A. Sweet Sparkling.	B. Sweet.	C. Dry.	D. Dry.	E. Renourri.
Number of samples contributing to average	5	4	30	15	10
Alcohol (by volume)	3·8	4·1	5·4	5·4	7·0
Extract (dried at 100° C.)	6·41	6·40	3·03	2·95	2·22
Ash	0·29	0·28	0·27	0·26	0·24
Acidity (as H_2SO_4)	0·36	0·39	0·52	0·58	0·54
Sugar	3·47	3·75	0·65	0·58	0·27
Polarimetric indication	−1°11′	—	−0° 12′	−0° 04′	−0° 02′
Alcohol after complete fermentation	5·9	6·3	5·8	5·7	7·1
Extract ,, ,, ,,	3·04	2·74	2·48	2·47	2·05
Original solids of juice (Allen) ...	12·77	13·24	11·97	11·90	13·76

The following figures show the extreme and mean composition of the sixty-four *ciders* included in the above table:

TABLE VIII.

	Minimum.	Maximum.	Average.
Alcohol (by volume) after complete fermentation	3·8	8·0	6·0
Extract, after complete fermentation	1·71	4·50	2·47
Ash	0·17	0·35	0·27
Acidity (as H_2SO_4)	0·27	0·71	0·52
Original solids of juice	—	—	12·39

The sample containing only 1·71 of extract was a *renourri* cider. In the greater number of cases the extract was considerably higher. The ash was usually notably higher than 0·17, the sample yielding this exceptionally small proportion showing 6·3 of alcohol (calculated) after complete fermentation.

The following figures show the average composition of *pure ciders* from various parts of France analysed in the Paris Municipal Laboratory:

TABLE IX.

	Well-fermented Cider.	Sweet Cider.
Alcohol, per cent. by volume	5·2	1·7
Solids, grammes per 100 c.c.	4·12	6·69
Sugar ,, ,, ...	0·89	2·91
Ash ,, ,, ...	0·29	0·26

From these results the Paris authorities ruled that pure, well-fermented ciders of the ordinary type should contain :

	Average.	Minimum.
Alcohol, per cent. by volume	5 to 6	3·0
Extract, grammes per 100 c.c.	3·0	1·8
Ash ,, ,, ...	0·28	0·17

Analyses of ciders from various parts of France, by G. Lechartier (*Compt. rend.*, ciii., 1104) show considerable departure from the foregoing figures.

It must be borne in mind that low alcoholic strength implies a high extract, so that the figures representing the minimum limits will never be met with in the same cider.

Perry presents a very close general resemblance to cider, but has a sweeter taste. This is not due so much to a larger proportion of sugar as to the smaller proportion of malic acid, the presence of which in cider masks the taste of the sugar. Pears usually contain very little acid, but are often rich in tannin and mucilaginous matters ; and hence the fermented product is more difficult to deal with than one prepared from a mixture of apples with pears called in France *cidresse*. Pears intended for the production of perry should be aromatic, rich in sugar and tannin, moderately acid, and at the exact point of ripeness. A large portion of the perry produced in France is distilled for the production of spirit.

The following analyses of *sparkling perry* from Worcestershire and Devonshire were made in my laboratory. The analysis of Gloucestershire perry is by Mr. G. Embrey :

TABLE X.

	Worcestershire.	Devonshire.	Gloucestershire.
Specific gravity	1020·0	1021·0	1010·0
Alcohol, per cent. by weight ...	4·61	4·81	3·64
= Proof spirit per cent.	10·11	10·54	7·98
Total solids	6·51	6·49	4·50
Volatile acid (as acetic)	0·41	0·35	0·22
Fixed acid (as malic)	0·25	0·20	0·24
Glucose	2·71	3·60	0·36
Sucrose	none	0·31	—
Ash	0·40	0·28	0·30
Original solids	16·61	16·92	12·33

With regard to the sophistications of cider, by far the most usual is dilution with water either before or after fermentation. How far it is legitimate to treat the once-pressed marc with water, and, after again pressing, to add the washing so obtained to the pure juice, is open to question.

Tartaric and citric acid are sometimes added to cure diseases of cider, and in other instances preservatives are used.

With regard to preservatives, I may say that in English ciders made by large manufacturers I have not met with any salicylic acid, though it is said to be commonly used in cider of American origin. Another preservative said to be largely employed by cider manufacturers is boric acid. At the commencement of the investigation on which this paper is founded I found boric acid in every sample of cider I examined, and naturally supposed its use as a preservative to be very general; but an examination of the apples themselves showed that boric acid was a constituent of apples to such an extent as to be very misleading, if the fact of its natural presence were ignored. As it is, a very strong reaction with turmeric is obtainable from 20 grammes of cider, apple-juice, or from the fruit itself. Of course, boric acid has been recognised as a natural constituent in minute quantity in various plants. Thus, it has been found in all parts of the vine and in hops, but not in malt or barley. Gassend found it in grapes, apples, and in some pears, but not in all; and he states that it is absent from tea, saffron, and cows' milk. Hodder found it in fruits generally, Crampton denies its presence in apples or cider, while Jay states that cider and perry contain from 0·011 to 0·017 gramme per litre.

A considerable number of experiments on the presence of boric acid in apples and other fruit have been made in my laboratory by Mr. A. R. Tankard, who found it in all the apples examined, and also in pears, quinces, pomegranates and grapes. In a specimen of "Fox Whelp" apple the amount of boric acid was 0·0076 per cent.; in quince half as much again. In pears the proportion appears to be variable.

Considerable trouble has been taken to arrive at a satisfactory method of determining these small quantities of boric acid in the presence of excess of phosphates, etc., and a satisfactory process was only devised after a large number of experiments had been made. The process actually employed must form the subject of a subsequent paper.

Dilution of cider will generally be indicated by deficiency in the proportions of alcohol and extractive matters. This can be calculated by the method of Grignon already described, but an alternative and preferable plan is to calculate the original solids of the juice from the results of the analysis, thus:

Alcohol, per cent. by weight × 2·07 = sugar fermented ...	
Acetic acid found × 1·5 = sugar fermented	
Extractive matter in sample	
Sum = original solids of juice	

The original solids of unwatered cider when thus calculated rarely fall below 12 per cent. On the other hand, an excessive proportion of original solids points to an addition of saccharine matter.

A valuable corroboration of the deduction from the foregoing method is obtained by a determination of the ash of the cider. According to G. Embrey, this should range from 0·25 to 0·35 per cent., and should not fall below the former figure. In American ciders a larger proportion of ash is usually met with, but for French ciders the limit of 0·25 per cent. would be too high. The addition of mineral matters such

as alkaline carbonates, lime, or boric acid would tend to increase the ash, and thereby invalidate the inference.

In 1895, as a result of a careful investigation and consultation with the Pomological Society of France, the Bath and West and Southern Counties Society recommended that no cider should be considered genuine which did not contain at least 4 per cent. of alcohol by volume (= 7 per cent. of proof spirit). This provision is insufficient unless supplemented by a requirement as to sugar or extractive matter. Incompletely fermented (sweet) cider of excellent quality might readily fail to comply with the foregoing requirement,* although by fermentation of the residual sugar the matured product would contain nearer 6 than 4 per cent. of alcohol.

I have to acknowledge the valuable assistance received from Mr. Jas. Thompson and Mr. A. R. Tankard in the execution of the greater number of the numerous analyses made in connection with the enquiry.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOODS AND DRUGS ANALYSIS.

Rapid Detection of Formaldehyde in Articles of Food. C. Arnold and C. Mentzel. (*Chem. Zeit.*, 1902, xxvi., 246.)—A little phenylhydrazine hydrochloride is dissolved in 3 to 5 c.c. of the cold liquid which is to be tested, and 2 to 4 drops (not more) of a 5 to 10 per cent. solution of sodium nitroprusside are added; then 8 to 12 drops of 10 to 15 per cent. alkali hydroxide are run in one at a time, when, according to the amount of formaldehyde present, a blue or blue-gray colour appears immediately, which is permanent for some time. In the case of fats, 5 to 10 grammes are shaken at the melting-point with 10 c.c. of 80 to 95 per cent. alcohol, cooled, the solution filtered through a moist paper, and examined as before. Raw or boiled milk, containing 0·015 gramme of formaldehyde per litre, gives a distinct green; pure milk is only tinted yellow. 0·05 gramme per litre yields a fine blue. Raw chopped flesh, saturated with a 0·5 per cent. solution of formaldehyde, was extracted with double its volume of hot water; the expressed and filtered liquor gave the reaction well. It also succeeded after keeping the meat for a day. With fats the test indicates 0·3 gramme per kilo.

A still more delicate reaction is given by substituting potassium ferricyanide for the nitroprusside; this develops an intense scarlet in presence of formaldehyde, permanent for a day. Unlike the former test, this only succeeds in alcoholic liquids when enough water to hold the ferricyanide in solution is added. The second reaction is not to be recommended for the examination of milk; on flesh it is only to be used if the material is not reddened by blood-pigments. In all other cases it may be employed if the first test fails by excessive dilution. F. H. L.

* An excellent cider made by one of the leading manufacturers was disqualified some years since on this insufficient ground.

The Detection of Aloes in Pharmaceutical Preparations. E. Léger. (*Journ. Pharm. Chim.*, 1902, xv., 335.)—*Identification of the Type of Aloes.*—In order to identify aloes and to distinguish between those of the type of Cape aloes and those of Barbadoes or Curaçoa, the author makes use of Klunge's reaction in the following manner: A solution of 0·5 gramme of aloes in 100 c.c. of hot water is rapidly cooled in a current of cold water and filtered from the deposited resin, the filtration being accelerated by the addition of a little powdered talc.

The following tests are then applied to the clear yellow filtrate:

1. A few decigrammes of sodium peroxide are introduced little by little into 20 c.c. of the liquid, previously heated to 80° C. An immediate evolution of oxygen occurs, and the liquid becomes brown, subsequently changing to bright cherry-red on the further addition of peroxide. The author has identified various substances in the products of the reaction, but attributes the red coloration to the presence of the alo-emodin of Tschirch and Oesterle (*Ber. d. d. Pharm. Ges.*, viii., 174; *Archiv. der Pharm.*, ccxxxvii., 81).

2. A second portion of 20 c.c. of the filtrate is treated with 1 drop of a saturated solution of copper sulphate, which causes the yellow colour to become darker. One gramme of pure crystallized sodium chloride is next introduced, and then 10 c.c. of 90 per cent. alcohol, which dissolves the flocculent precipitate produced by the salt.

With Socotrine and Cape aloes a vinous red colour is obtained, which gradually fades, until after an hour the liquid has become yellow, and shows no further change. In the case of Barbados and Curaçoa aloes, however, a bright, currant-red coloration is obtained, which does not disappear even after standing for twelve hours. The author has found that this reaction is due to a special aloin, which he terms barbaloin, in the latter varieties of aloes.

Both of the above reactions are very sensitive, the first being obtained with solutions containing only 0·1 per cent. of aloes. Where the coloration is faint, the liquid should be acidified with hydrochloric acid and extracted with ether, and the ethereal solution of emodin shaken with 2 to 3 c.c. of water, rendered alkaline with sodium hydroxide, when a bright red colour will be obtained.

Detection of Aloes.—For the detection of aloes in pharmaceutical preparations the first (sodium peroxide) reaction is recommended. It frequently happens, however, that other drugs are also present, such as rhubarb, which contains chrysophanic acid (dioxymethylanthraquinone), an emodine (trioxymethylanthraquinone), and rheine (tetraoxymethylanthraquinone), which dissolve in sufficient quantity to falsify the results. The presence of oxymethylanthraquinones can be detected by adding a small quantity of sodium hydroxide solution, with which they give an immediate red coloration, whilst the solution of pure aloes remains yellow.

If the red colour be obtained, a slight excess of subacetate of lead is added to the solution to precipitate the oxymethylanthraquinones; or the following method of separation may be employed: Fifty c.c. of the filtered solution of 1 gramme of aloes in 100 c.c. of water are treated with 20 c.c. of a 5 per cent. solution of alum, then with ammonium hydroxide in excess, and lastly with acetic acid until the liquid is just acid. Twenty c.c. of the clear filtrate tested with sodium peroxide gives the

aloes reaction clearly, whilst rhubarb extract treated in the same way gives only a faint peach coloration.

As a general rule, however, the author recommends the precipitation with sub-acetate of lead, which he shows gives good results with mixtures of aloes with *Cascara sagrada* and with *Rhamnus frangula.* C. A. M.

On the Reactions for the Identification of Certain Drugs. E. Bourquelot. (*Journ. Pharm. Chim.*, 1902, xv., 342-345.)—*Aloes.*—Klunge's reaction (see preceding abstract) having been shown to be one of oxidation, the author has made experiments to determine whether the same red coloration could be obtained by the action of oxidizing enzymes. For this purpose he used a 50 per cent. glycerin extract of *Russula delica,* and obtained a pronounced purple-red colour on adding 10 to 20 drops of this extract to 20 c.c. of a solution of aloin (1 : 500). As in the case of Klunge's reaction, the intensity of the coloration obtained diminished on recrystallization of the aloin, until eventually there was no reaction, owing to the elimination of the barbaloin.

Tyrosine.—Hirschsohn's reagents for aloin (copper sulphate and hydrogen peroxide) also react with tyrosine, a brown coloration being obtained on heating the solution with 1 drop of a 1 per cent. solution of copper sulphate and 2 drops of hydrogen peroxide solution.

Loganine—the glucoside discovered by Dunstan and Short—is present in tinctures of nux vomica and St. Ignatius' bean. The residue left on evaporating a few drops of the tincture in a porcelain basin, and warmed with 3 drops of dilute sulphuric acid (1 : 3), assumes a reddish-violet colour.

Preparations of Opium.—In order to identify the presence of meconic acid, 2 c.c. of the tincture are mixed with 4 c.c. of water and a few drops of hydrochloric acid, the mixture shaken with ether, and the ethereal extract shaken with 2 to 3 c.c. of water and a drop of ferric chloride, a red colour being produced in the aqueous layer.

Tincture of Cachou.—In the new German Pharmacopœia this is stated to give a deep red colour when heated with potassium chromate solution. As the tincture itself is very dark, the author modifies the test by boiling together 20 c.c. of water, 10 drops of the tincture, and 5 drops of potassium chromate solution (1 : 20), a cherry red colour being immediately produced. C. A. M.

TOXICOLOGICAL ANALYSIS.

Differentiation of Human Blood from the Blood of Animals. De Nobele. (*Ann. Soc. Med. de Ghent*, 1901, 331; through *Ann. de Chim. anal.*, 1902, vii., 150-152.)—The author has studied the method devised by Wassermann and Schütze, who found that the serum of a rabbit or a mouse into which human serum had been injected gave a precipitate when mixed with the serum of human blood.

He has proved that the injection of different human excreted liquids, such as the sera of milk, saliva, pus, albuminous urine, or ascitic fluid, has also the same effect

upon the serum of the animal, which in each case gives a precipitate with human blood, but not with the blood of different animals.

Reactions were also obtained with decomposed human blood. Thus, stains on linen from several days to two months in age, when treated with very dilute sodium chloride solution or with sodium hydroxide solution (0·1 per cent.), gave solutions yielding a precipitate with the injected serum. No reaction was given, however, by a stain nine years old.

To determine the action of heat, drops of blood were heated on glass to temperatures of 75°, 100°, and 125° C., and the dried residues dissolved in sodium chloride solution and tested. Reactions were obtained with the blood dried at the lower temperatures, but not with that dried at 125° C.

Attempts to prepare a specific serum by feeding the animal with human serum instead of by inoculation were unsuccessful.

Corin (*Ann. Soc. Med. legal. Belg.*, i. [13]) has found that the active agent in the injected serum is a paraglobulin, which can be precipitated with magnesium sulphate. The precipitate, collected on a filter and dried, can be kept unaltered, and when required can be redissolved.

According to the author, the serum can also be evaporated under reduced pressure without losing its activity. The dried residue is preserved in sealed tubes in the dark, and has been found to react as strongly as the original liquid after six months (*cf.* ANALYST, xxvii., 157). C. A. M.

Comparison of the Stas-Otto and Kippenberger Methods of detecting Alkaloids in Toxicology. J. Weiss. (*Münch. medicin. Wochenschr.*, 1902, xlix., 367; through *Chem. Zeit. Rep.*, 1902, 100.)—The author has carried out experiments on the detection of strychnine, morphine, and atropine in nutritive liquors, in the stomachs and intestines of corpses, and in whole corpses, soon after death and also a considerable time after burial. In all cases the yield of alkaloid was greater by the Stas-Otto than by the Kippenberger process. It is therefore better to employ the former for the isolation of the substance, and only to use Kippenberger's method with iodine and potassium iodide for quantitative purposes. F. H. L.

ORGANIC ANALYSIS.

Colour Reaction for Wood-Fibre. A. Kaiser. (*Chem. Zeit.*, 1902, xxvi., 335.)—Equal volumes of amyl alcohol, free from furfural, and strong sulphuric acid are warmed on the water-bath to about 90° C., until a slight evolution of gas occurs; the faintly orange mixture is then cooled. This reagent, which may be termed "amyl-sulphuric acid," has the property of turning wood-fibre red, violet, or dark indigo-blue, according to the quantity present. Newspaper or pine shavings moistened therewith strike first a greenish, afterwards a bright blue colour; while pure Swedish filter-paper only becomes red and commoner qualities violet. Appearance of the tint is hastened by a current of air and by gentle warming. As the colours vary with the

quantity, it is possible roughly to gauge the proportion of wood-fibre present in a sample of paper. The whole process is an adaptation of Vitali's reaction.

F. H. L.

The Alkalinity of Crude Sugar. Herberger. (*Centralbl. Zuckerind.*, 1902, x., 552; through *Chem. Zeit. Rep.*, 1902, 92.)—The author states that phenolphthalein is useless for determining the alkalinity of crude sugar, since various salts and organic substances are present in the material which cause it to appear acid when it is really alkaline. F. H. L.

Quantitative Estimation of Arabinose. C. Neuberg and J. Wohlgemuth. (*Zeits. physiol. Chem.*, 1902, xxxv., 31; through *Chem. Zeit. Rep.*, 1902, 108.)—In the course of a research in which large quantities of the three arabinoses and their derivatives were required, the authors tested the following method. One hundred c.c. of urine, to which 1 gramme of arabinose had been added, was acidified with two drops of 30 per cent. acetic acid, concentrated on the water-bath to 40 c.c., and treated with 40 c.c. of hot 96 per cent. alcohol. After cooling for two hours the deposited salts were filtered off and washed with 40 c.c. of 50 per cent. spirit. The filtrate was mixed with 1·4 grammes of diphenylhydrazine, warmed in a boiling water-bath for half an hour, allowed to stand for twenty-four hours, and then filtered through a Gooch crucible, using the liquor for rinsing purposes. The crystals were then washed with 30 c.c. of 30 per cent. alcohol, which left them brilliantly white. The crucible was heated in the drying oven at 80° C. to constant weight, when the hydrazone assumed a faint violet tint, and the yield was found to be 2·1055 grammes of hydrazone, corresponding with 0·9993 gramme of *l*-arabinose, or 99·93 per cent. of the theoretical. Similar tests with *d*-arabinose gave a return of 99·80 per cent., and with *i*-arabinose 100·06 per cent. The method is therefore available for the separation of this sugar from other carbohydrates, especially xylose, even when the latter is present in considerable excess. It is necessary that 1 per cent. of arabinose be present; weaker liquids must be previously concentrated *in vacuo*. F. H. L.

On Stahre's Reaction for Citric Acid. A. Wöhlk. (*Zeit. anal. Chem.*, 1902, xli., 77-100.)—The sensitive reaction for citric acid discovered by Stahre (*Nordisk Farm. Tidsskrift*, 1895, ii., 141) is based upon the fact that on oxidizing citric acid with potassium permanganate and adding bromine a white precipitate insoluble in ether is obtained. Stahre concluded that in this reaction the citric acid was oxidized to acetone, which was converted by the bromine into a bromacetone.

In applying the test when less than 5 milligrammes of citric acid are present, the acid is dissolved in 2 c.c. of water, and heated to 30° C. after the addition of 2 to 4 drops of $\frac{N}{10}$ permanganate solution. If any slight precipitation of manganese peroxide occur, 1 or 2 drops of a 4 per cent. solution of ammonium oxalate and about 1 c.c. of 10 per cent. sulphuric acid are introduced to clear the liquid. On now adding 2 drops of bromine water a distinct turbidity is produced.

When more than 5 milligrammes of citric acid are present the solution in 2 c.c. of water is treated with 5 drops of the permanganate solution, heated to 30° to 40° C., cooled, and mixed with 1 c.c. of dilute sulphuric acid. Should any precipitate be formed it can be removed by the addition of a little ammonium oxalate. Bromine water then added drop by drop gives a precipitate of extremely fine needles of pentabromacetone.

Stahre's reaction is obtained not only with pure solutions of citric acid and its salts, but also in the presence of other organic acids precipitated by calcium, such as tartaric, oxalic, malic acids, or inorganic acids, such as sulphuric and phosphoric acids. In such cases, however, more permanganate must be used, and it is best to make the test on a hot solution. Organic acids that react with bromine must obviously be removed.

The author confirms the statements of Henkel, Scheibe, and others as to the presence of citric acid as a normal constituent of milk. He has separated a compound which he has identified as citric acid by Stahre's reaction and other tests.

C. A. M.

The Determination of Mustard Oil. P. Rœser. (*Journ. Pharm. Chim.*, 1902, xv., 361-364.)—The method recommended by the author is based upon the conversion of the allyl isothiocyanate into thiosinamine (as in the methods of Gadamer, etc.), adding standard silver nitrate solution to the ammoniacal liquid, and titrating the excess of silver by Denigés' method.

Five c.c. of a 1 per cent. solution of the commercial essence are mixed with 10 c.c. of ammonium hydroxide, and, after dilution with water, shaken with 10 c.c. of $\frac{N}{10}$ silver nitrate solution. After standing for twenty-four hours, the liquid is made up to 100 c.c. and filtered, 50 c.c. of the filtrate treated with 5 c.c. $\frac{N}{10}$ potassium cyanide solution, and the excess of cyanide titrated with silver nitrate solution, a few drops of a slightly ammoniacal 5 per cent. solution of potassium iodide being used as indicator.

The number of c.c. of silver nitrate solution taken up by the sulphur, doubled and multiplied by the factor 0·3137, gives the percentage of mustard oil in the essence.

For the determination of mustard oil in mustard flour, leaves, etc., 5 grammes of the sample are mixed with 60 c.c. of water and 15 c.c. of 60 per cent. alcohol, and distilled after standing for two hours. The distillate is received in a flask containing 10 c.c. of ammonium hydroxide, and after two-thirds of the liquid have passed over, it is mixed with 10 c.c. of $\frac{N}{10}$ silver nitrate solution and diluted to 100 c.c., and the determination completed as described above.

It is stated that this method gives results almost identical with those obtained by the methods of Dieterich and Gadamer. C. A. M.

Quantitative Separation of Cholesterin from Fats. E. Ritter. (*Zeits. physiol. Chem.*, 1902, xxxiv., 430; through *Chem. Zeit. Rep.*, 1902, 100.)—The author has submitted his own process (this vol., p. 16) and that proposed by Bömer to a comparison, using in each case a fat relatively rich in phytosterin. He finds that his own method returns rather more phytosterin than Bömer's process, and considers that many of the objections to the latter are avoided. The product is also purer, but it is not absolutely pure phytosterin. F. H. L.

The Composition of Cacao Butter. J. Klimont. (*Monatsh. für Chem.*, 1902, xxiii., 51-59.)—This paper is a continuation of the author's former communication on this subject (ANALYST, xxvii., 15), in which he stated that he had identified tripalmitin, tristearin, and a mixed glyceride containing the radicles of oleic, palmitic, and stearic acids, together with another mixed glyceride.

From a consideration of the elementary composition, iodine value, and saponification value of this last glyceride he has come to the conclusion that it contains the radicals of myristic, palmitic, and oleic acid, and possibly of some still lower fatty acids.

Neither arachidin nor arachidic acid could be detected in the specimen of fat examined. C. A. M.

A Note on the Use of the Bechi or Silver Nitrate Test on Olive Oils. L. M. Tolman. (*Journ. Amer. Chem. Soc.*, xxiv., 396.)—Since some olive oils free from cottonseed oil give a brown coloration with the Bechi test as generally applied, the author recommends the following preliminary treatment, which, whilst not affecting the reducing action of the cottonseed oil, removes the free acid and other products of rancidity of the olive oil: To 25 c.c. of the oil, 25 c.c. 95 per cent. alcohol are added, and the whole is gently heated and then vigorously shaken; after allowing the liquids to separate, the alcoholic solution is decanted off, and the residue washed first with 2 per cent. nitric acid and finally with water. For the test, 10 c.c. oil, 10 c.c. amyl alcohol, and 5 c.c. of the reagent (2 grammes silver nitrate dissolved in 200 c.c. alcohol, with the addition of 40 c.c. ether and 2 drops nitric acid), are mixed in a test-tube. Half the mixture is kept for comparison, the other half being heated for ten minutes in a boiling water-bath. The above method of purification is stated to give very satisfactory results, and can be readily applied to lard and other fats. A. G. L.

Comparison of Methods used to Determine the Iodine Value of Oils. F. W. Hunt. (*Journ. Soc. Chem. Ind.*, 1902, xxi., 454.)—The methods compared were those of Hübl, Wijs, and Hanus (see ANALYST, xxvii., 15). He found that the Wijs solution (ICl in glacial acetic acid) lost 3 per cent. of its strength in two weeks, and the Hanus solution (IBr in glacial acetic acid) nearly 5 per cent. In determining

the iodine values, Hübl's solution was allowed to act for five hours, the other two for one hour. Each determination was done in duplicate:

	Hübl.	Hanus.	Wijs.
Pale seal	117·5	120·7	124·8
Whale	120·2	120·6	123·7
Olive	82·3	81·9	83·4
Castor (cold drawn)	82·6	84·4	85·6
Dogfish liver	134·7	141·2	143·2
Arachis (earth-nut)	91·8	91·6	93·4
Arctic shark	89·0	93·8	98·9
Pale rape	103·0	101·9	102·1
Coast cod	148·5	147·5	154·6
Newfoundland cod	144·8	150·0	154·7
Linseed	174·8	174·5	177·3
Cottonseed	108·5	107·0	110·0

The Wijs solution gave results higher than the Hübl solution, especially in the case of fish oils. The Hanus solutions gave results which were in some cases intermediate and in others agreed with those given by Hübl's solution.

Experiments were also made using a solution of iodine monobromide in carbon tetrachloride. The results obtained were:

	Iodine Value.	Corrected for Substitution.
Olive oil	82·0	—
Coast oil	153·9	—
Linseed	179·7	177·8
Arachis	90·8	89·5
Pale seal	125·4	124·5

The author does not recommend this solution, however. A. M.

On the Temperature Reaction of Oils with Sulphuric Acid—Maumené's Test. H. C. Sherman, J. L. Danziger, and L. Kohnstamm. (*Journ. Amer. Chem. Soc.*, xxiv., 266.)—The authors have investigated the sources of errors in Maumené's test, especially as regards the drying oils, which give a violent reaction with the sulphuric acid, and come to the conclusion that if the oil is diluted with some non-drying oil the value calculated is always too high. They find that the use of a somewhat more dilute acid (89 to 90 per cent.) than is usually employed gives good results, which are directly comparable for both drying and non-drying oils. They recommend the statement of all results as "specific temperature reactions," according to the suggestion of Thomson and Ballantyne (*Journ. Soc. Chem. Ind.*, x., 233), which are obtained by multiplying the observed rise of temperature by 100, and dividing by the rise observed when 50 grammes water are treated with 10 c.c. of the same acid under the same conditions. Contrary to Thomson and Ballantyne, however, they find this value is slightly lower for a more dilute acid; but, still, their results agree reasonably well with those obtained by these authors. A. G. L.

Metallic Soaps from Linseed Oil. An Investigation of their Solubilities in Certain of the Hydrocarbons. Hermann T. Vulté and Harriet Winfield Gibson. (*Journ. Amer. Chem. Soc.*, xxiv., 215.)—The authors have investigated the solubilities of a number of metallic soaps from linseed oil in various petroleum solvents and in turpentine, as well as the permanence of the solutions, and give tables showing the results obtained. They find that the lead soap separates from its solutions in all the petroleum solvents in less than one hour, the nickel soap only after several days, the iron soap only on the application of a gentle heat, and that the manganese soap is unique as regards its drying properties They also find that no one solvent can be recommended for all the soaps, there being a maximum solubility for each one in some special solvent. A. G. L.

Characteristics of Butter from Human Milk. Sauvaitre. (*Ann. de Chim. nal.*, 1902, vii., 143-145.)—The author has obtained the following results with a specimen of human butter, and compares the figures with those given by a sample of cow's butter:

	Cow's Butter.	Human Butter.
Specific gravity at $\frac{100°}{15°}$ C.	0·866 per cent.	0·870 per cent.
Critical temperature of solution in absolute alcohol	56° C.	59° C.
Coefficient of solubility in absolute alcohol	43·3 per cent.	34·7 per cent.
Melting-point of insoluble fatty acids ...	40·5° C.	40° C.
Solidification-point ,, ,, ...	39° C.	37° C.
Saponification value	221·2 per cent.	218·4 per cent.
Reichert-Wollny value	26·3 ,,	15·8 ,,
Hehner value	87·2 ,,	89·2 ,,
Iodine value	35·51 ,,	43·37 ,,
Total volatile acids	6·69 ,,	4·41 ,,
Ratio of butyric acid to caproic acid ...	2·2 : 1	2·4 : 1
Unsaponifiable matter	1·58 per cent.	4·68 per cent.
Melting-point of unsaponifiable matter ...	139° C.	143° C.

C. A. M.

Detection of Indican in Urine. Bertault. (*Journ. Pharm. Chim.*, 1902, [6], xv., 277; through *Chem. Zeit. Rep.*, 1902, 92.) If the urine contains iodine (or bromine) as well as indican, the well-known test must be modified as follows: After the sample has been treated with an equal volume of hydrochloric acid, a few c.c. of chloroform, and a few drops of sodium hypochlorite, the acidified urine is pipetted off, the tube containing the chloroform is washed with water to remove the bulk of the acid, and then potassium hydroxide is added to alkalinity. The violet colour produced by the iodine disappears, and the chloroform remains blue if indican is present, or colourless in its absence. F. H. L.

Valuation of Rubber Goods. A. Heintz. (*Chem. Zeit.*, 1902, xxvi., 247.)—The author suggests a method for the valuation of rubber goods, in which an attempt

is made, by ultimate analysis, to determine the proportion of true caoutchouc present. After a qualitative examination, the various foreign organic substances are removed by treatment with Henriques' solvents: unsaponifiable oils by ether, asphaltum by nitrobenzene, "substitutes" by alcoholic soda. The last traces of these liquids are next most carefully washed away, the residue is thoroughly dried, a combustion is carried out, and the amount of caoutchouc is estimated from the gain of the sulphuric acid tube, on the assumption that the body remaining after the above process is represented by the formula $(C_{10}H_{16})_n$. The method is not offered as an exact process, but one for commercial purposes only. It suffers from two possible sources of error: (1) That the caoutchouc originally used in the manufactured goods does not correspond in composition with the formula quoted, but contains some oxygen compound, resins, etc.; (2) that the solvents do not remove the whole of, or remove substances other than, those they are supposed to extract. As regards the first point, analysis of the washed rubber employed in the manufacture of boots has shown that on an average it consists of 97 per cent. of $(C_{10}H_{16})_n$, so that even if the finished wares contained 50 per cent. of caoutchouc, which is unlikely, the error would be only 1·5 per cent. In order to settle the second point, analyses have been made of several trade samples of finished goods and of materials prepared specially for the author, both by his process and by that of Henriques, etc. Two samples of Russian-made shoes gave 57·63 and 60·43 per cent. of inorganic matter, 1·51 and 1·57 per cent. of sulphur, 19·23 and 18·62 per cent. of organic substance, or 21·63 and 19·38 per cent. of caoutchouc, by difference respectively. By the author's process they gave 20·23 and 18·65 per cent. of caoutchouc, or, after correction for the 3 per cent. of oxygenated matter, 20·84 and 19·21 per cent. A material composed of ceresin and brown "substitutes," beside the rubber and sulphur, gave 75·11 per cent. (corrected) on ultimate analysis, whereas it contained 76·75 per cent.* of caoutchouc. Another specimen containing inorganic matter, beside the sulphur and caoutchouc, gave 49·65 per cent. on combustion, the actual amount of rubber being 49·30 per cent.* F. H. L.

The Determination of Sulphur in Plants. G. S. Fraps. (*Journ. Amer. Chem. Soc.*, xxiv., 346.)—To 5 grammes of the material, placed in a 3½-inch porcelain dish, 20 c.c. concentrated nitric acid are gradually added; the mixture is heated cautiously on the water-bath, then concentrated, and, after the addition of 10 c.c. of a 5 per cent. solution of potassium nitrate, evaporated to dryness; the residue is ignited, at first gently, finally over the blast-lamp, and the sulphur in it estimated as usual.

A. G. L.

INORGANIC ANALYSIS.

The Electrolytic Determination of Copper in Iron. H. Koch. (*Zeit. anal. Chem.*, 1902, xli., 105-107.)—The copper is first concentrated by treating the iron with dilute sulphuric acid and then separated by electrolyzing the insoluble residue.

* It is not clear whether by these figures the author means the yield of the Henriques process, or whether they are the proportion of caoutchouc actually employed by the manufacturer.—F. H. L.

In the case of steel, 100 grammes of the shavings are treated with 400 c.c. of dilute sulphuric acid (specific gravity, 1·06), half of this quantity being first used without the aid of heat, and the remainder added to the hot liquid after completion of the reaction. Crystallization of the sulphates during cooling is prevented by the addition of 500 c.c. of water.

The black residue is collected on a double filter, dried, ignited, and dissolved in a large porcelain crucible in a few c.c. of concentrated hydrochloric acid, and the solution evaporated to dryness after the addition of sulphuric acid. The residue is dissolved in about 20 c.c. of water and the same quantity of nitric acid (specific gravity 1·20), the solution filtered, and the filtrate diluted with water to about 120 c.c.

A few drops of a 5 per cent. solution of oxalic acid are then added, and the liquid electrolyzed for nine to ten hours with a current of about 0·094 ampère per square centimetre. The positive electrode consists of a spiral of platinum wire 1·3 millimetres thick, which rests upon the bottom of the beaker, whilst the negative electrode is a cylinder of platinum foil 9 by 3·5 centimetres in size.

The method requires a slight modification in the case of gray pig-iron, owing to the large proportion of graphitic carbon present protecting the iron from the action of the acid. To obviate this the residue should once more be boiled with about 200 c.c. of sulphuric acid (sp. gr. 1·06) for about thirty minutes before being treated as described above. C. A. M.

Rapid Method for the Volumetric Determination of Molybdenum Steel. Francis T. Kopp. (*Journ. Amer. Chem. Soc.*, xxiv., 186.)—Half a gramme of the sample is dissolved in 2 c.c. sulphuric acid (specific gravity 1·58) and 12 c.c. water in a platinum crucible of 100 c.c. capacity, solution being hastened by heating. The solution is then evaporated until white fumes are given off, and cooled ; to the residue 30 grammes fused potassium bisulphate are added, and the whole is then gently heated to a red heat, and kept at this temperature for ten or fifteen minutes. After cooling, the melt is dissolved in 500 c.c. hot water, the solution cooled, transferred to a litre flask, and, after the addition of 100 c.c. ammonia (specific gravity 0·90), made up to the mark with water. After mixing thoroughly 500 c.c. are filtered through a dry filter, 40 c.c. sulphuric acid (specific gravity 1·58) added, and the solution is run through a Jones reductor consisting of a column of zinc 12 inches long and 0·5 inch diameter. To the reduced solution 10 c.c. sulphuric acid are added, and the molybdenum is titrated with standard permanganate solution. A blank, consisting of 450 c.c. water, 50 c.c. ammonia, and 40 c.c. sulphuric acid, should be run through the reductor and titrated as above, in order to ascertain the error due to impurities in the zinc.

For tungsten steels, 1 gramme of the sample is dissolved in 25 c.c. dilute nitric acid, with the addition, after violent action is over, of 10 c.c. strong hydrochloric acid. The solution is evaporated to dryness, the residue baked, and then re-dissolved in 15 c.c. hydrochloric acid. The tungsten will be precipitated as tungsten trioxide. After cooling and diluting with water to 100 c.c., 50 c.c. of the solution are filtered through a dry filter, 10 c.c. of sulphuric acid are added, and the solution (which should be free from tungsten) is evaporated till white fumes are given off, transferred

to a platinum crucible, again evaporated till white fumes are given off, cooled, and fused with 30 grammes potassium bisulphate, as in the case of steels.

For ferro-molybdenums 0·5 gramme of the sample is dissolved in 15 c.c. strong nitric acid in a platinum crucible; when thoroughly dissolved, 2 c.c. sulphuric acid are added, the solution is evaporated till white fumes are given off, and then treated as for steels.

The method gave good results when checked on steels containing known amounts of molybdenum, and also when compared with other methods of estimating molybdenum. A. G. L.

Identification of Metals of the Platinum Group by means of Sodium Peroxide. Leidié and Quennessen. (*Bull. Soc. Chim.*, 1902, xxvii., 179-183.)—Various tests are commonly employed to differentiate the metals of platinum ores, and some of these are both tedious and also require fresh samples of the material to be taken.

The authors have made experiments to devise a rapid method in which all the tests can be applied to one and the same sample, and have eventually found that sodium peroxide at a dull red heat is a suitable reagent.

The metal, which should be in the finely divided state as obtained by ignition of the salt in hydrogen, is mixed with five or six times its weight of sodium peroxide, and gently heated in a nickel basin over a low gas flame. The mass first blackens and then becomes pasty, but after being stirred with a platinum spatula, and the heating continued, it becomes semi-liquid. The flame is now withdrawn, and the cold contents of the basin cautiously treated with water in the proportion of ten to twelve times the weight of sodium peroxide used. The mixture is now transferred to a tube, and, after standing, the clear liquid is decanted, and the deposit mixed with water and collected on a filter.

The oxide of nickel formed will be found in this deposit, and if insoluble oxides or insoluble alkaline salts of the platinum group are also present, it can be readily separated from them by means of the nitrite method previously described by Leidié (Analyst, xxvi., 108).

The separate metals treated with sodium peroxide in this way give the following results:

Osmium is completely converted into sodium osmiate, $OsO_2(NaO)_2$, which dissolves in water, yielding a yellow solution. On passing a current of chlorine through this solution slightly heated, osmium peroxide, OsO_4, can be collected in a receiver immersed in ice water. The latter compound may be identified by the formation of potassium osmiate (action of potassium nitrite on heating, or of alcohol and potassium hydroxide in the cold).

Ruthenium is completely converted into sodium peruthenate, $RuO_3(NaO)$, which in the presence of water yields the ruthenate, $RuO_2(NaO)_2$. The latter forms an orange solution, which on treatment with chlorine gas, as above, yields a yellow liquid, in which ruthenium peroxide, RuO_4, may be identified by the reduction of ruthenium on treatment with potassium hydroxide and alcohol in the cold, or by the formation of a brown sesquichloride, Ru_2Cl_6, by the action of hot hydrochloric acid.

Palladium yields an alkaline palladate soluble in water. On neutralizing the yellow solution with hydrochloric acid and then evaporating it after the addition of potassium chloride and nitric acid, ruby red crystals of potassium chloro-palladate, insoluble in a saturated solution of potassium chloride, are formed.

Iridium is converted into a basic iridate, $IrO_3.4Na_2O$, which on treatment with water yields a blue solution. On adding a slight excess of hydrochloric acid to this solution, and evaporating after the further addition of potassium chloride and a little nitric acid, black crystals of potassium chloro-iridate are obtained. These are also insoluble in a saturated solution of potassium chloride.

Platinum is converted into the insoluble sodium platinate, which remains on the filter with the nickel oxide. The precipitate is dissolved in strong hydrochloric acid, the greater part of the acid subsequently evaporated, sodium nitrite added until the liquid is neutral, then sodium carbonate, and the liquid boiled and filtered. Nickel carbonate remains on the filter, whilst the filtrate contains the double nitrite of platinum and sodium. On evaporating this filtrate to dryness after the addition of hydrochloric acid, the residue dissolved in water and treated with ammonium chloride gives the characteristic crystals of ammonium chloro-platinate.

Rhodium is converted partially into the dioxide, RhO_2, soluble in hot concentrated hydrochloric acid, and partially into a sesquioxide, remaining undissolved. The filtrate obtained by treating the mass with hot hydrochloric acid will also contain the nickel. It is treated in the same manner as the platinum solution, and filtered from the nickel carbonate. On heating the filtrate with an excess of hydrochloric acid it becomes rose-coloured from the formation of the double chloride, $Rh_2Cl_6.6NaCl$, but does not yield a precipitate with ammonium chloride.

The following scheme shows the course to be followed in a systematic qualitative analysis:

The product of the action of sodium peroxide upon the metal is treated with water, yielding a solution and a precipitate

A. The solution is coloured

Blue. It is neutralized with HCl, and evaporated with HNO_3 and KCl. Black crystals insoluble in KCl indicate IRIDIUM.

Yellow. It is heated and treated with a current of chlorine.

A substance is volatilized, giving a black precipitate with $(NH_4)_2S$.

Nothing volatilizes. The liquid is neutralized with HCl, and evaporated with HNO_3 and KCl. Red crystals insoluble in KCl indicate PALLADIUM.

The solution distilled gives an insoluble violet osmiate with KOH and alcohol, or KNO_3 on heating. No brown coloration with hot HCl. OSMIUM.

The solution distilled gives a black precipitate with KOH and alcohol. With hot HCl it gives a brown coloration. RUTHENIUM.

The solution is light yellow, and gives a precipitate with NH_4Cl, insoluble in excess of NH_4Cl. PLATINUM.

The solution is red, and gives no precipitate with NH_4Cl. RHODIUM.

B. The solution is colourless. It is rejected. The precipitate is treated with HCl, the liquid filtered and treated with $NaNO_2$ and Na_2CO_3.

The filtered liquid is treated with HCl in excess and evaporated to dryness, and the residue dissolved in water.

C. A. M.

A Note on the Determination of Molybdenum in Steel. George Auchy. (*Journ. Amer. Chem. Soc.*, xxiv., 273.)—Not more than 1·308 grammes of the steel are treated with a large excess of strong nitric acid, with the addition of a little potassium chlorate if chromium is present; the nitric acid is evaporated off, the residue boiled with strong hydrochloric acid, evaporated to dryness to separate silica, taken up with strong hydrochloric acid, and the solution evaporated to the first appearance of a scum. To the solution 5 c.c. hydrochloric acid, diluted to 20 c.c. with water, are added, and after solution is complete the volume of the liquid is made up to 50 c.c. with water, and the solution poured little by little, with constant shaking, into a solution of 20 grammes caustic soda in 100 c.c. water, contained in a 300-c.c. flask. The liquid is made up to the mark with water, mixed, and 250 c.c. are filtered off, acidified with sulphuric acid, boiled down to less than 100 c.c., reduced with zinc, and titrated with permanganate. A blank must be made on a steel free from molybdenum, the same amount of hydrochloric acid and of chromium being present as in the actual determination. Most of the chromium is precipitated with the iron, but a small amount remains in solution. The method gives good results, the caustic soda separation being sufficiently exact for all practical purposes.

A. G. L.

The Analysis of Metallic Molybdenum and its Lower Oxides. C. Friedheim and M. K. Hoffmann. (*Berichte*, 1902, xxxv., 791-795.)—The pure molybdenum dioxide used by the authors in their experiments was prepared by reducing molybdenum trioxide for five to seven hours in a current of hydrogen at a temperature of 450° C, and then heating the mixture of dioxide and unreduced trioxide to a dull red heat in a current of dry hydrochloric acid gas so as to volatilize the trioxide in the form of chloride.

For the determination of the molybdenum dioxide in an insoluble molybdenum oxide the substance is slowly heated to the boiling-point with a sufficient quantity of a 10 per cent. solution of ferric ammonium sulphate and twice that amount of dilute sulphuric acid (1 : 5).

The molybdenum is dissolved in accordance with the equation

$$Fe_2(SO_4)_3 + MoO_2 + H_2O = 2FeSO_4 + H_2SO_4 + MoO_3,$$

and by titrating the amount of ferrous salt with standard permanganate the quantity of molybdenum dioxide can be obtained.

In the case of an oxide containing lower oxides of molybdenum soluble in water the substance is treated with an excess of acid potassium permanganate solution, and the excess titrated with standard oxalic acid solution.

Metallic molybdenum may be analysed by the ferric ammonium sulphate method described above, or the following indirect gravimetric method may be used: The metal, or the compound containing lower oxides, is heated for about an hour, with continual shaking on the water-bath, with a very dilute ammoniacal solution of silver sulphate. After standing for twelve hours, air being excluded, the separated silver is collected on a filter, washed with a very slightly ammoniacal 10 per cent. solution of ammonium nitrate, dissolved off the filter by means of dilute nitric acid, and determined either gravimetrically or volumetrically.

C. A. M.

Colorimetric Estimation of Sulphur in Cast Iron. T. Naske. (*Stahl und Eisen*, 1902, xxii., 333; through *Chem. Zeit. Rep.*, 1902, 92.)—Lindlay has described a process for the estimation of sulphur which depends on the fact that in presence of ferric chloride and sulphuretted hydrogen *p*-phenylenedimethyldiamine hydrochloride is converted into methylene blue. The sulphur of the iron is therefore to be liberated with hydrochloric acid, the gas passed into sodium hydroxide, and a colorimetric operation carried out. Naske, however, objects to this method that acid produces methyl sulphide as well as sulphuretted hydrogen, that on absorption in caustic soda normal sulphide, hydrosulphide, and polysulphides are formed, that the hydrogen sulphide is not quantitatively taken up, and that the sodium sulphide solution gradually changes into thiosulphate and sulphate. On the other hand, solutions of methylene blue are decomposed—*i.e.*, decolorized—by sulphuretted hydrogen and thiosulphate. Lindlay's process is accordingly only suitable for qualitative purposes, and the same remarks apply to the employment of Lauth's violet, which he has also recommended. F. H. L.

An Accurate Estimation of Sulphur in Iron by the Evolution Method. Harry E. Walters and Robert Miller. (*Proc. Eng. Soc. West. Pennsylvania*, xviii., 83.)—In this method 5 grammes of the sample are weighed out into a porcelain or copper boat, which is then placed in a porcelain or nickel combustion-tube, and heated to bright redness for fifteen to thirty minutes in a current of natural gas or hydrogen. After allowing it to cool in the current of gas, the sample is removed, transferred to a flask, and the hydrogen sulphide evolved as usual by means of hydrochloric acid (1 acid : 1 water). The evolved gases are absorbed in ammoniacal cadmium chloride solution and titrated with iodine. The results given by this method were checked against those given by the ordinary evolution method and by a gravimetric method, and are almost identical with the latter, the largest difference being 0·004 per cent. in about thirty determinations, whilst the ordinary evolution method in many cases gave very low results. For an ordinary pig-iron fifteen minutes' heating is sufficient; for samples containing titanium it is necessary to heat for half an hour. A. G. L.

The Determination of Sulphur in Iron Pyrites. R. Auzenat. (*Ann. de Chim. anal.*, 1902, vii., 93, 94.)—The following method is recommended as giving accurate results in a much shorter time, and with less attention to the evaporation, than those obtained by Lunge's method: About 0·5 gramme of the finely powdered mineral, previously dried at 100° C., is weighed into a flask, into which are then introduced successively 20 c.c. of a 10 per cent. solution of sodium chloride, 10 c.c. of hydrochloric acid, sp. gr. 1·18, and 10 c.c. of nitric acid, sp. gr. 1·5. As soon as effervescence has ceased, the flask is placed in an oil bath provided with a thermoregulator, and the liquid evaporated to dryness. Under these conditions the temperature can be raised to 120° C. without the liberation of free sulphuric acid.

The author's comparative determinations have shown that it is possible to save several hours in this way without fear of loss. C. A. M.

Rapid Method for Estimating Thorium in Monazite Sand. E. Benz. (*Zeits. für angew. Chem.*, 1902, xiii., 309.)—Half a gramme of the finely divided sand is intimately mixed in a platinum crucible with the same quantity of sodium fluoride and 10 grammes of potassium pyrosulphate and gradually heated. When the evolution of gas ceases the crucible is raised to a low red heat and kept at it for fifteen minutes. The melt is extracted first with dilute, then with concentrated hydrochloric acid. The solution is filtered. The filtrate is nearly neutralized with ammonia, taking care not to produce a permanent precipitate. It is raised to boiling, and 3 to 5 grammes of solid ammonium oxalate are added with stirring. The oxalates fall as a granular precipitate. A little ammonium oxalate solution is added to make sure that the precipitation is complete. After standing all night the oxalates are filtered off, then washed with as little water as possible into a porcelain basin. The filter is washed with hot concentrated nitric acid and water, and the liquid is evaporated almost to dryness. A few c.c. of concentrated nitric acid are added and then 20 c.c. of fuming nitric acid, the basin is covered with a watch-glass and placed upon the water-bath. When the effervescence ceases the liquid is evaporated to dryness; some water is added and again evaporated off. The residue is then dissolved in water and ammonium nitrate solution is added; the liquid is warmed to 60° or 80°, and 20 c.c. of distilled hydrogen peroxide (2 or 3 per cent.) are added. A precipitate of thorium peroxide is formed, which may be coloured yellow by minute traces of cerium peroxide. This is washed with hot water containing some ammonium nitrate, and when half dry is ignited in a platinum crucible and weighed as ThO_2.

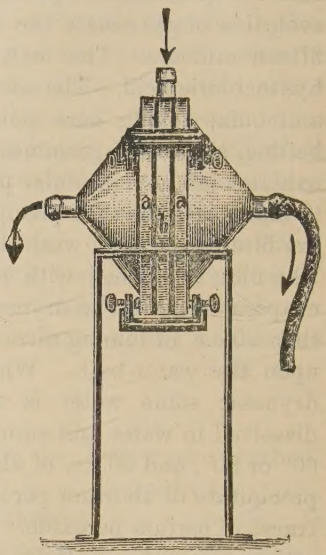
A. M.

A Rotary Cement Kiln for Use in the Laboratory. E. D. Campbell. (*Journ. Amer. Chem. Soc.*, xxiv., 249.)—The author describes a small rotary furnace for cement burning which gave very satisfactory results. The furnace itself consists of an 8-inch steam-pipe 32 inches long, the lining being made of four sections of magnesite tubes packed into the steel jacket with asbestos, the asbestos being mixed at one end for a distance of 2 inches with fire-clay and sodium silicate. The rotary is turned by means of a one-seventh horse-power electric motor, and heated by means of a Hoskins hydrocarbon burner. The temperature is controlled by means of a Le Chatelier thermocouple, the wires of which pass through a double-bored porcelain tube covered for a distance of 8 inches with platinum foil. A fixed couple is kept at a point 3·5 inches from the hot end, and the temperature at other points is taken by means of a moving couple. The hottest zone is at a distance of 6 inches from the discharge end. The temperature at this point can be raised up to 1,630° C., which is too high for most mixtures. About 4,500 grammes of material are usually used for one run, yielding 2,500 to 2,800 grammes clinker, at the rate of about 600 to 700 grammes clinker per hour from the first appearance of clinker to the time feeding is stopped.

A. G. L.

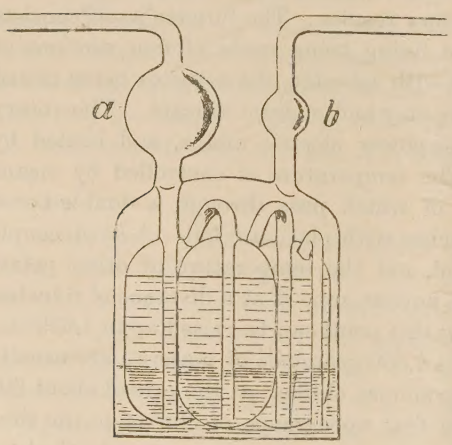
APPARATUS.

A Laboratory Filter-press. (*Chem. Zeit.*, 1901, xxv., 1162.)—This apparatus consists of a pair of porcelain cones, with leading tubes at the apices and with flat, perforated plates at the bases. Between them is clamped a porcelain ring or distance-piece, square in section, and provided with an entrance tube. To put the apparatus together, one cone is held point downwards on a suitable stand, a piece of filter-cloth or asbestos is laid on the perforated plate, then a rubber-washer is put in position, next the distance-piece, next a second cloth and rubber ring, and finally the other cone is applied, and the whole clamped up. In use it is supported as shown, the turbid liquid entering through a tube about 1·5 metres high to give the requisite pressure. The liquid then filters right and left through the cloths. To wash the precipitate, the apparatus is supported in the other position, the entry tube being closed, and water being forced in at one apex only. By adjusting a Liebig condenser round the pipe through which the thick liquor is being admitted, filtration may be conducted in the warm. Clearly the apparatus can be employed with suction instead of with pressure. It is patented, and may be obtained from Kaehler and Martini of Berlin, W.



F. H. L.

A New Potash Apparatus. **A. Landsiedl.** (*Oesterr. Chem. Zeit.*, 1902, v., 30.)—The construction of this apparatus is fully explained by the accompanying diagram. It will be seen that the stream of gas has to pass through the potassium hydroxide contained in the three inner vessels, and then through that in the outer bottle. The device is filled through *b* by suction, and emptied through *a* by blowing. By sucking sharply at *b* the whole of the potash may be drawn into the outer vessel and so mixed together, being then driven back into its proper position by a cautious aspiration at *a*. It is claimed for the apparatus that it is easy to clean, very compact, and that it stands firmly. It is protected in Germany, and may be procured from the firm of V. E. Zahradnik, 5, Krongasse, Vienna, V.



F. H. L.

ERRATUM.

This volume, page 87, fourth line from bottom, *for* "100 c.c." *read* "1,000 c.c."